# Ruthenium-Catalyzed Enantioselective Ring-Closing Metathesis

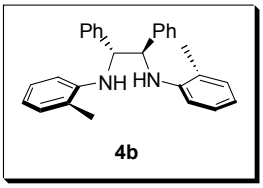
*T. Jon Seiders, D. William Ward, and Robert H. Grubbs*

*Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125*

**[Supplementary Information]**

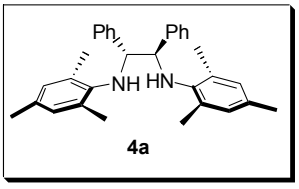
**General Procedures**. When specified, manipulation of organometallic compounds was performed using standard Schlenk techniques under an atmosphere of dry argon or in a nitrogen-filled Vacuum Atmospheres drybox ($O_2$ < 2 ppm). NMR spectra were recorded on a Varian Inova (499.85 MHz for $^{1}H$; 202.34 MHz for $^{31}P$; 125.69 MHz for $^{13}C$) or a Varian Mercury 300 (299.817 for $^{1}H$; 121.39 MHz for $^{31}P$; 74.45 MHz for $^{13}C$). $^{31}P$ NMR spectra were referenced using $H_3PO_4$ ($\delta$ = 0 ppm) as an external standard.

**Materials and Methods**. Toluene, dichloromethane, tetrahydrofuran, and benzene were dried by passage through solvent purification columns. Silica gel was obtained from TSI.



4b

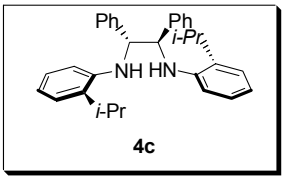
**Representative Preparation of Compound 4b.** Under inert atmosphere, palladium acetate (0.016 g, 0.071 mmol), BINAP (0.088 g, 0.14 mmol), and sodium *t*-butoxide (0.410 g, 4.26 mmol) were added to toluene (25 mL) and stirred for 20 min. (R,R)-diphenylethylenediamine (0.300 g, 1.42 mmol) and 2-bromotoluene (0.510 g, 2.98 mmol) were then added and the solution was heated to 100 °C for 16 hours. The solution was then cooled to ambient temperature, diluted with hexanes (75 mL), and filtered through a plug of silica. The silica was washed with methylene chloride to elute the product. The volatiles were removed *in vacuo* to yield a white solid (0.52 g, 93%). mp 49-51°C. $[\alpha]^{22}_{D}$ +18.6 ° (c 0.5, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): δ 2.15 (s, 6H), 4.73 (s, 2H), 6.33 (bs, 2H), 6.62 (t, *J*=7.5 Hz, 2H), 6.91 (t, *J*= 7.8 Hz, 2H), 7.01 (d, *J*=7.2 Hz, 2H), 7.25 (m, 10H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 17.7, 63.9, 111.8, 117.6, 122.9, 126.8, 127.0, 127.6, 128.5, 129.9, 139.7, 144.7. FAB HRMS [M+H] *m/z*: found 393.2319, calcd ($C_{28}H_{29}N_2$) 393.2331. Anal. Calcd for $C_{28}H_{28}N_2$: C, 85.67, H, 7.19, N, 7.14. Found C, 85.52, H, 7.31, N, 7.03.



4a

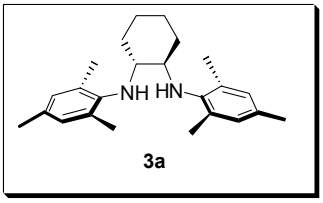
Compound **4a.** (80 %). mp 65-67 °C. $[\alpha]^{22}_{D}$ –7.5 ° (c 0.5, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): δ 2.10 (s, 12H), 2.15 (s, 6H), 3.99 (s, 2H), 4.78 (s, 2H), 6.69 (s, 4H), 6.84 (m, 4H), 7.12 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 19.5,

20.5, 66.5, 127.0, 127.6, 128.3, 128.6, 129.6, 130.3, 140.5, 141.5. FAB HRMS [M+H] *m/z*: found 449.2969, calcd ($C_{32}H_{37}N_2$) 449.2957.



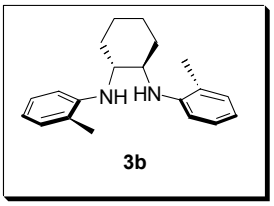
**4c**

Compound **4c.** (70 %). mp 86-88 °C. $[\alpha]^{22}_D$ +16.9 ° (c 0.5, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): δ 1.15 (d, *J*=6.9 Hz, 6H), 1.30 (d, *J*=6.9 Hz, 6H), 2.89 (s, *J*=6.9 Hz, 2H), 4.74 (s, 2H), 6.29 (d, *J*=8.1 Hz, 2H), 6.69 (t, *J*=7.2 Hz, 2H), 6.88 (d, *J*=7.2 Hz, 2H), 7.11 (d, *J*=7.5 Hz, 2H), 7.2-7.3 (m, 10H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 22.5, 23.4, 27.5, 63.9, 112.4, 117.8, 124.7, 126.3, 126.9, 127.6, 128.6, 133.0, 139.9, 143.3. FAB HRMS [M+H] *m/z*: found 449.2962, calcd ($C_{32}H_{37}N_2$) 449.2957.



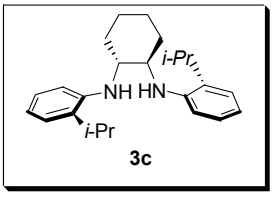
**3a**

Compound **3a**. (53%). mp 122 °C. $[\alpha]^{22}_D$ +37 ° (c=1.05, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): δ 1.17 (br, 4H), 1.62 (br, 2H), 1.83 (br, 2H), 2.24 (s, 6H), 2.31 (s, 12H), 3.06 (br, 2H), 3.40 (br, 2H), 6.82 (s, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 19.34, 20.72, 25.03, 32.87, 62.26, 129.61, 130.85, 131.27, 142.13. IR (KBr, $cm^{-1}$) 584.3, 726.3, 753.2, 852.4, 1222.6, 1448.5, 1480.0, 2852.7, 2925.9, 3320.3, 3449.4. FAB HRMS [M+] *m/z*: found 350.2718, calcd ($C_{24}H_{34}N_2$) 350.2722.



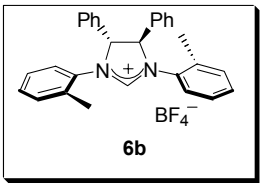
3b

Compound **3b.** (67%) mp 84 °C. $[\alpha]^{22}_{D}$= -27 ° (c=0.94, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): δ 1.2-1.6 (br m, 4H); 1.81 (br, 2H); 2.01(s, 6H); 2.38 (d, *J*=12.3 Hz, 2H); 3.35 (br, 2H); 3.7 (br, 2H); 6.68 (t, *J*=7.2 Hz, 1H); 6.75 (d, *J*=6.6 Hz, 1H); 7.05 (d, *J*=7.2 Hz, 1H); 7.14 (t, *J*=8.1 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 17.79, 24.93, 32.99, 57.85, 110.52, 117.27, 122.98, 127.21, 130.57, 145.99. IR (KBr, $cm^{-1}$) 745.3, 982.2, 1039.4, 1050.8, 1115.0, 1141.2, 1257.5, 1310.0, 1500.3, 1605.0, 2848.7, 2949.8, 3394.0. FAB HRMS [M+] *m/z*: found 294.2091 calcd ($C_{20}H_{26}N_2$) 294.2096. Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.59; H, 8.90; N, 9.51. Found C, 81.71; H, 8.93; N, 9.38.



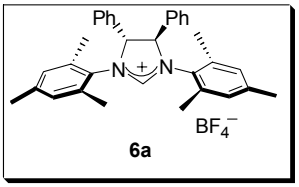
3c

Compound **3c.** (70%). $[\alpha]^{22}_{D}$= -30.0 ° (c=0.59, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): δ 1.10 (d, *J*=6.9 Hz, 6H); 1.19 (d, *J*=6.6 Hz, 6H); 1.2-1.5 (br m, 4H); 1.81 (br m, 2H); 2.40 (d, *J*=12.9 Hz, 2H); 2.72 (m, *J*=6.6 Hz, 2H); 3.36 (d, *J*=8.1Hz, 2 H); 3.89 (br s, 2H); 6.76 (br s, 4H); 7.13 (br m, 4H) $^{13}$C NMR (125 MHz, $CDCl_3$): δ 22.43, 22.56, 24.95, 27.12, 32.83, 57.84, 111.25, 117.62, 125.42, 126.75, 133.28, 144.53. IR (neat, $cm^{-1}$) 745.3, 1038.7, 1162.0, 1254.4, 1302.1, 1359.6, 1453.8, 1513.7, 1583.0, 1602.5, 2860.1, 2959.6, 3036.4, 3064.4, 3424.7. FAB HRMS [M+] *m/z*: found 350.2714 calcd ($C_{24}H_{34}N_2$) 350.2722.



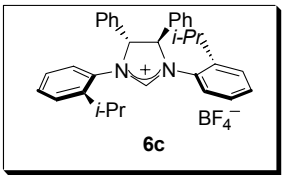
**6b**

**Representative Preparation of Compound 6b.** Diamine **4b** (0.290 g, 0.74 mmol), ammonium tetrafluoroborate (0.093 g, 0.89 mmol), and triethyl orthoformate (1 mL) were heated to 120 °C for 5 hours. The solution was then allowed to cool to ambient temperature, and the product was precipitated and washed 3 times with diethyl ether (3 X 10 mL). The solids were dissolved in methylene chloride and filtered, and the volatiles were removed *in vacuo* to yield an off-white solid (0.360 g, 99%). mp 188-191°C. $[\alpha]^{22}_{D}$ +32.2 ° (c 0.5, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 6H), 5.78 (s, 2H), 7.17 (m, 6H), 7.39 (m, 12H), 8.32 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 18.5, 76.1, 127.6, 127.7, 128.0, 129.6, 130.0, 130.2, 131.6, 132.5, 133.3, 133.4, 157.3. FAB HRMS [M+(-$BF_4$)] *m/z*: found 403.2159, calcd ($C_{29}H_{27}N_2$) 403.2174.



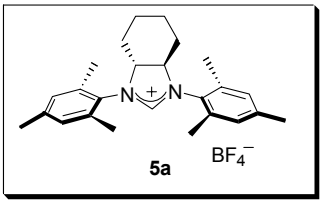
**6a**

Compound **6a.** (70%). mp 127-130°C. $[\alpha]^{22}_{D}$ +23.7 ° (c 0.5, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): δ 1.93 (s, 6H), 2.23 (s, 6H), 2.67 (s, 6H), 5.98 (s, 2H), 6.75 (s, 2H), 6.98 (s, 2H), 7.37 (m, 10H), 7.39, 8.65 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 18.3, 19.1, 21.1, 72.9, 128.5, 128.8, 129.4, 130.1, 130.7 (2), 131.5, 134.0, 136.1, 140.3, 158.2. FAB HRMS [M+ (-$BF_4$) ] *m/z*: found 459.2812, calcd ($C_{33}H_{35}N_2$) 459.2800.



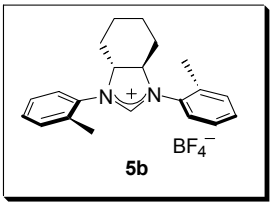
**6c**

Compound **6c.** (73%). mp 115-118 °C. $[\alpha]^{22}_{D}$ +27.8 ° (c 0.5, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): δ 1.18 (d, *J*= 6.6 Hz, 6H), 1.33 (d, *J*= 7.2 Hz, 6H), 3.13 (sept, *J*= 6.9 Hz, 2H), 5.79 (s, 2H), 7.2-7.5 (m, 16H), 7.58 (d, *J*= 8.1 Hz, 2H), 8.25 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 24.1, 24.7, 28.7, 77.1, 126.7, 127.7, 128.3, 128.5, 129.6, 130.3 (2), 130.7, 132.7, 144.4, 157.3. FAB HRMS [M+(-$BF_4$)] *m/z*: found 459.2800, calcd ($C_{33}H_{35}N_2$) 459.2800.



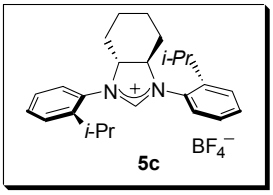
**5a**

Compound **5a**. (99%) mp 187 °C. $[\alpha]^{22}_{D}$ +29.7 ° (c 1.04, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CD_2Cl_2$): δ 1.33-1.44 (br m, 2H); 1.66-1.84 (br m, 2H); 1.94-2.10 (br m, 4H); 2.30 (s, 6H); 2.35 (s, 6H); 2.37 (s, 6H); 4.10 (br m, 2H); 7.04 (s, 2H); 7.08 (s, 2H); 8.24 (s, 1H). $^{13}$C NMR (125 MHz, $CD_2Cl_2$): δ18.17, 18.85, 21.33, 24.20, 27.94, 71.50, 129.42, 130.56, 130.71, 135.17, 136.68, 141.45, 161.20. IR (KBr, $cm^{-1}$): 519.2, 578.2, 742.5, 848.0, 939.3, 1063.6, 1168.8, 1235.3, 1251.7, 1272.6, 1388.4, 1451.6, 1482.3, 1578.8, 1613.5, 2951.9, 3049.1, 3422.9. FAB HRMS [M+(-$BF_4$)] *m/z*: found 361.2641, calcd ($C_{25}H_{33}N_2$) 361.2644.



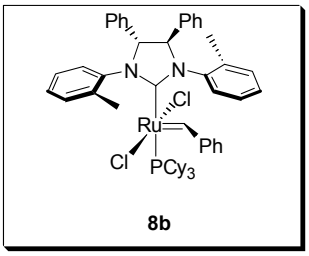
**5b**

Compound **5b**. (90%) mp 213 °C. $[\alpha]^{22}_{D}$ +33.5 ° (c 0.97, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CD_2Cl_2$): δ 1.41(br m, 2H); 1.79 (br m, 2H); 1.99 (br m, 2H); 2.12 (br d, *J*= 11.1 Hz, 2H); 2.41 (s, 6H); 4.21 (br m, 2H); 7.42 (m, 8H); 8.16 (s, 1H). $^{13}$C NMR (125 MHz, $CD_2Cl_2$): δ 18.11, 24.15, 27.87, 71.77, 127.36, 128.29, 130.92, 132.42, 133.39, 134.99, 159.72. IR (KBr, $cm^{-1}$): 524.0, 766.7, 1066.6, 1162.5, 1256.0, 1303.0, 1450.2, 1496.6, 1573.6, 1595.4, 2874.5, 2961.9, 3072.2, 3441.3. FAB HRMS [M+(-$BF_4$)] *m/z*: found 305.2018, calcd ($C_{21}H_{25}N_2$) 305.2018.



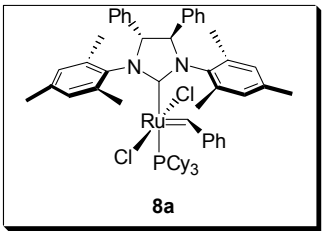
**5c**

Compound **5c**. (93%). mp 205 °C. $[\alpha]^{22}_{D}$ +20.4 ° (c 1.0, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CD_2Cl_2$): δ 1.23-1.46 (br m, 16H); 1.92-2.18 (br m, 4H); 2.6-3.5 (br m, 2H); 3.7-4.6 (br m, 2H); 7.37-7.44 (br m, 3H); 7.44-7.60 (br m, 5H); 8.00 (s, 1H). $^{13}$C NMR (125 MHz, $CD_2Cl_2$): spectrum is broad, 23.49, 24.10, 24.85, 27.72, 28.86, 72.38, 126.81, 127.86, 128.17, 129.86, 131.53, 146.22, 159.72. IR (KBr, $cm^{-1}$) 498.6, 557.1, 598.3, 768.5, 1050.1, 1162.6, 1248.1, 1449.2, 1491.5, 1574.2, 1596.6, 2870.2, 2965.9, 3066.8, 3422.8. FAB HRMS [M+(-$BF_4$)] *m/z*: found 361.2647; calcd ($C_{25}H_{33}N_2$) 361.2644.



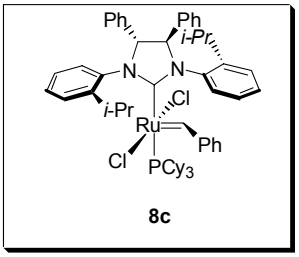

**8b**

**Representative Preparation of Complex 8b**. In a glove box, imidazolium salt **6b** (0.200 g, 0.408 mmol) and potassium hexafluoro-*t*-butoxide (0.108 g, 0.490 mmol) were dissolved in tetrahydrofuran (4 mL), added to a solution of bis(tricyclohexylphosphine)-benzylidene ruthenium dichloride (0.403 g, 0.490 mmol) in toluene (10 mL), and transferred to a schlenk flask. The flask was removed from the glove box and heated to 50 °C under argon for 2 hours. The solution was cooled to ambient temperature and the volatiles were removed *in vacuo*. The product was purified by column chromatography ($SiO_2$, 7:1 pentane:$Et_2O$) to yield a brown microcrystalline solid (0.300 g, 78%). mp 142-144 °C (dec.). $[\alpha]^{22}_D$ +6.0 ° (c 0.005, $CH_2Cl_2$). $^1$H NMR (500 MHz, $CDCl_3$) exists as a mixture of atropisomers (3.2:1): δ 0.9-2.9 (m, ArCH(C*H*$_3$)$_2$ + P*Cy*$_3$), 5.01 (bs, NC*H*Ph,), 5.17 bs, NC*H*Ph), 6.5-7.6 (m, Ar*H*), 8.15 (bs, *o*-Ar*H* of benzylidene), 19.41 (s, Ru=C*H*Ph), 19.46 (s, Ru=C*H*Ph). $^{13}$C NMR (125 MHz, $C_6D_6$): δ 221.0 (N*C*N), 297.3 (N*C*N Ru=*C*HPh). $^{31}$P NMR (121 MHz, $C_6D_6$): δ 26.96. IR (KBr, cm$^{-1}$) 3059, 3030, 2925 (s), 2849 (s), 1493 (s), 1446 (s), 1419 (s), 762, 743, 721, 710. ES HRMS [M-Cl]$^+$ *m/z*: found 909.3647, calcd ($C_{54}H_{65}ClN_2PRu$) 909.3647. Anal. Calcd for $C_{54}H_{65}Cl_2N_2PRu$: C, 68.63, H, 6.93, N, 2.96. Found C, 69.19, H, 7.01, N, 3.03.




**8a**

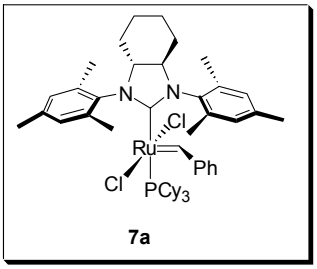
Complex **8a**. (0.300 g, 78%). mp 140-142 °C (dec.). $[\alpha]^{22}_{D}$ –0.6 ° (c 0.005, $CH_2Cl_2$). $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) exists as a mixture of atropisomers (1.1:1): δ 0.9-3.1 (broad multiplets, ArCH($CH_3$)$_2$ + P$Cy_3$), 5.5-7.5 (broad multiplets, Ar*H*), 9.0 (broad singlet), 19.10 (s, Ru=C*H*Ph), 19.25 (s, Ru=C*H*Ph). $^{13}C$ NMR (125 MHz, $C_6D_6$): δ 223.7 (bs, N*C*N), 295.6 (Ru=*C*HPh), 296.6 (Ru=*C*HPh). $^{31}P$ NMR (121 MHz, $C_6D_6$): δ 29.16. IR (KBr, $cm^{-1}$) 2924 (s), 2850 (s), 1446 (s), 1401, 1378, 1237 (s), 736, 697. ES HRMS $[M\text{-}Cl]^+$ *m/z*: found 965.4232, calcd ($C_{58}H_{73}ClN_2PRu$) 965.4257. Anal. Calcd for $C_{58}H_{73}Cl_2N_2PRu$: C, 69.58, H, 7.35, N, 2.80. Found C, 69.79, H, 7.61, N, 2.59.




**8c**

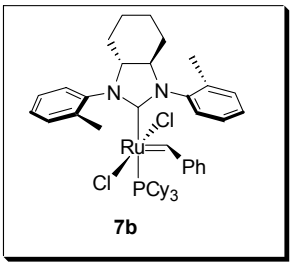
Complex **8c**. (0.300 g, 78%). mp 150-155 °C (dec.). $[\alpha]^{22}_{D}$ +21.0 ° (c 0.005, $CH_2Cl_2$). $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) exists as a mixture of atropisomers (27:1): δ 0.9-1.9 (m, ArCH($CH_3$)$_2$ + P$Cy_3$), 3.53 (m, ArC*H*($CH_3$)$_2$), 3.76 (m, ArC*H*($CH_3$)$_2$), 4.92 (d, *J*=4Hz, NC*H*Ph,), 5.23 (d, *J*=4Hz, NC*H*Ph), 6.6-7.6 (m, Ar*H*), 8.59 (d, *J*=7 Hz), 19.25 (s, Ru=C*H*Ph), 19.34 (s, Ru=C*H*Ph). $^{13}C$ NMR (125 MHz, $C_6D_6$): δ 220.2 (d, *J*=75.6 Hz, N*C*N), 298.2 (N*C*N Ru=*C*HPh). $^{31}P$ NMR (121 MHz, $CD_2Cl_2$): δ 24.9. IR (KBr, $cm^{-1}$) 3060, 2926 (s), 2849 (s), 1489 (s), 1448 (s), 1417 (s),

758 (s), 702 (s). ES HRMS $[M\text{-}Cl]^+$ *m/z*: found 965.4283, calcd ($C_{58}H_{73}ClN_2PRu$) 965.4257. Anal. Calcd for $C_{58}H_{73}Cl_2N_2PRu$: C, 69.58, H, 7.35, N, 2.80. Found C, 70.27, H, 7.64, N, 2.61.



**7a**

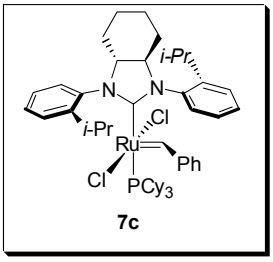
Complex **7a.** (80%). $[\alpha]^{22}_D$ = +100.5 ° (c= 0.19, $CH_2Cl_2$). $^1H$ NMR (500 MHz, $CD_2Cl_2$ (27:1): δ 0.60-1.52 (br m, 34 H); 1.53 (d, *J*= 1Hz, 6H); 1.62-1.80 (br m, 3H); 1.90 (s, 3H); 1.91-2.25 (br m, 4H); 2.30 (s, 3H); 2.33-2.78 (br m, 6H); 3.47-4 (br m, 2H); 5.77 (br s, 1H); 6.62-7.45 (br m, 7H); 8.97 (br s, 1H); 19.00 (s, 1H);. $^{13}C$ NMR (125 MHz, $C_6D_6$): δ 225.52 (br, N*C*N); 294.07, 294.35 (Ru=*C*HPh). $^{31}P$ NMR (121 MHz, $CD_2Cl_2$): δ 30.02. IR (KBr, $cm^{-1}$) 687.0, 848.2, 897.6, 1135.8, 1257.7, 1360.0, 1384.5, 1445.4, 1480.1, 2850.8, 2925.1, 3437.8. ES HRMS $[M\text{-}Cl]^+$ *m/z*: found 867.4092, calcd ($C_{50}H_{71}ClN_2PRu$) 867.4098.



**7b**

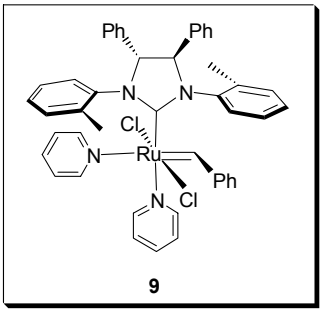
Complex **7b.** (73%). $[\alpha]^{22}_D$ = -68 ° (c= 0.05, $CH_2Cl_2$). $^1H$ NMR (500 MHz, $CD_2Cl_2$ ) exists as a mixture of atropisomers: δ 0.72-2.29 (br m, 45 H); 2.49-2.78 (br m, 2H); 3.35-4.05 (br m, 2H); 5.92-8.33 (br m, 13 H); 18.93-19.03 (br m, 1H). $^{13}C$ NMR (125 MHz, $CD_2Cl_2$): δ 227.61 (d, *J*= 73 Hz, N*C*N); 296.40 (br s,

Ru=*C*HPh). $^{31}$P NMR (121 MHz, $CD_2Cl_2$): δ 25.60, 27.95, 28.83. IR (KBr, $cm^{-1}$) 678.5, 721.7, 1147.4, 1261.9, 1446.2, 1491.8, 1636.6, 2849.6, 2925.7, 3447.9. ES HRMS [M-Cl]$^+$ *m/z*: found 811.3456, calcd ($C_{46}H_{63}ClN_2PRu$) 811.3470.



**7c**

Complex **7c**. (75%). $[\alpha]^{22}_D$ = -120 ° (c= 0.05, $CH_2Cl_2$). $^1$H NMR (500 MHz, $CD_2Cl_2$ ) exists as a mixture of atropisomers (4.9:1): δ 0.80-2.01 (br m, 53 H); 3.07-4.00 (br m, 4H); 6.04-8.48 (m, 13H); 19.04 (s, 0.83 H); 19.21 (s, 0.17 H). $^{13}$C NMR (125 MHz, $CD_2Cl_2$): δ 274.00 (d, *J*= 78 Hz, N*C*N); 298.51 (br s, Ru=*C*HPh). $^{31}$P NMR (121 MHz, $CD_2Cl_2$): δ 23.85, 25.70, 29.65. IR (KBr, $cm^{-1}$) 678.1, 756.0, 848.6, 897.1, 1259.7, 1447.4, 1489.6, 1559.4, 1653.8, 2849.5, 2925.1, 3447.4. ES HRMS [M-Cl]$^+$ *m/z*: found 867.4080, calcd ($C_{50}H_{71}ClN_2PRu$) 867.4098.



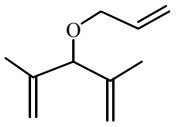
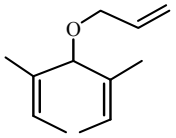
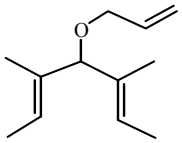
**9**

**Preparation of 9**. Pyridine (0.20 mL) was added to a solution of **8b** (0.050 g, 0.053 mmol) in toluene (0.5 mL). The solution was stirred at ambient temperature for 15 minutes during which time the color changed from red-brown to bright green. After ~ 30 minutes a green precipitate formed. Pentane was added to

further precipitate the product. The mother liquor was decanted and the green solid was washed 3 times with pentane (2 mL) and dried *in vacuo* (0.040 g, 92%). $[\alpha]^{22}_{D}$ -45.0 ° (c 0.005, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$) exists as a mixture of atropisomers (2.5:1): δ 1.73 (s, ArC*H*$_3$, 3H), 2.66 (s, ArC*H*$_3$, 3H), 2.78 (s, ArC*H*$_3$, 3H), 2.97 (s, ArC*H*$_3$, 3H), 5.29 (d, *J*=4 Hz, NC*H*Ph, 1H), 2.40 (d, *J*=7 Hz, NC*H*Ph, 1H), 5.53 (d, *J*=4 Hz, NC*H*Ph, 1H), 5.74 (d, *J*=7 Hz, NC*H*Ph, 1H), 6.2-8.6 (Ar*H*, 31H), 9.81 (dd, *J*=7.5, 1.5, 2H), 9.97 (m, 2H), 19.33 (s, 1H), 19.35 (1H). $^{13}$C NMR (125 MHz, $C_6D_6$): δ 219.5 (N*C*N), 220.5 (N*C*N), 317.3 (Ru=*C*HPh), 318.3 (Ru=*C*HPh). IR (KBr, cm$^{-1}$) 3136, 3107, 3060, 3028, 2934, 2876, 1492 (s), 1445 (s), 1378 (s), 1249 (s), 1220 (s), 756 (s), 706 (s). Anal. Calcd for $C_{46}H_{42}Cl_2N_4Ru$: C, 67.15, H, 5.14, N, 6.81. Found C, 67.24, H, 5.29, N, 6.80.

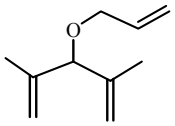
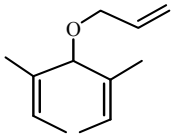
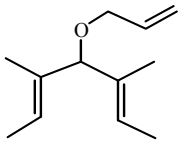
**Representative Procedure for the Desymmetrization of Achiral Trienes.** In a 10 mL schlenk flask on the bench top, tetrahydrofuran (2.0 mL) was added to catalyst **8c** (0.0050 g, 0.0050 mmol). Sodium iodide (0.015 g, 0.100 mmol) was added and the solution was stirred at ambient temperature for 1 hour. All of the salts were observed to dissolve and the color turned from reddish-brown to brown. Substrate **11** (0.020 g, 0.11 mmol) and toluene (10 μL internal standard) were added via syringe and the solution was heated at 35 °C for 2 hours after which time the solution darkened considerably. An aliquot was taken and analyzed by chiral GC for enantiomeric excess and conversion.

Desymmetrization of achiral trienes **10-12** by catalysts**7a-c**

| Substrate | Catalyst | Additive | ee %[a] | Conversion % |
|---|---|---|---|---|
|  **10** | **7a** | none | 8 | 93 |
| | **7b** | none | 3 | >95 |
| | **7c** | none | 5 | >95 |
| | **7a** | NaI | 5 | 20 |
| | **7b** | NaI | 5 | 46 |
| | **7c** | NaI | 5 | 42 |
|  **11** | **7a** | none | 4 | >95 |
| | **7b** | none | 5 | 44 |
| | **7c** | none | 6 | 94 |
| | **7a** | NaI | 1 | >95 |
| | **7b** | NaI | 5 | >95 |
| | **7c** | NaI | 10 | >95 |
|  **12** | **7a** | none | 9 | >95 |
| | **7b** | none | 0 | >95 |
| | **7c** | none | 11 | >95 |
| | **7a** | NaI | 13 | 20 |
| | **7b** | NaI | 13 | >95 |
| | **7c** | NaI | 3 | >95 |

[a]The **R** enantiomer is the major product in all entries exhibiting significant enantiomeric excesses.

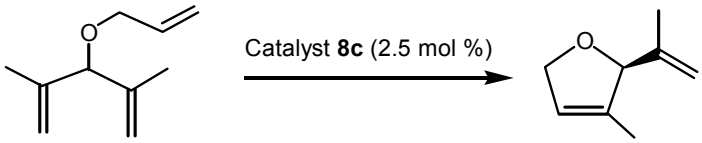
Desymmetrization of achiral trienes **10-12** by catalyst **8a-c**

| Substrate | Catalyst | Additive | ee %[a] | Conversion % |
|---|---|---|---|---|
|  **10** | **8a** | none | 13 | 57 |
| | **8b** | none | 23 | 95 |
| | **8c** | none | 23 | 96 |
| | **8a** | NaI | 5 | 28 |
| | **8b** | NaI | 38 | 18 |
| | **8c** | NaI | 39 | 20 |
|  **11** | **8a** | none | <2 | 65 |
| | **8b** | none | <2 | 80 |
| | **8c** | none | 12 | 97 |
| | **8a** | NaI | <2 | 43 |
| | **8b** | NaI | 17 | 78 |
| | **8c** | NaI | 35 | 90 |
|  **12** | **8a** | none | 15 | 67 |
| | **8b** | none | 28 | 64 |
| | **8c** | none | 35 | 82 |
| | **8a** | NaI | 17 | 39 |
| | **8b** | LiBr | 63 | 90 |
| | **8b** | NaI | 85 | 91 |
| | **8c** | LiBr | 69 | 90 |
| | **8c** | NaI | 90 | 82 |

[a] The **S** enantiomer is the major product in all entries exhibiting significant enantiomeric excesses.

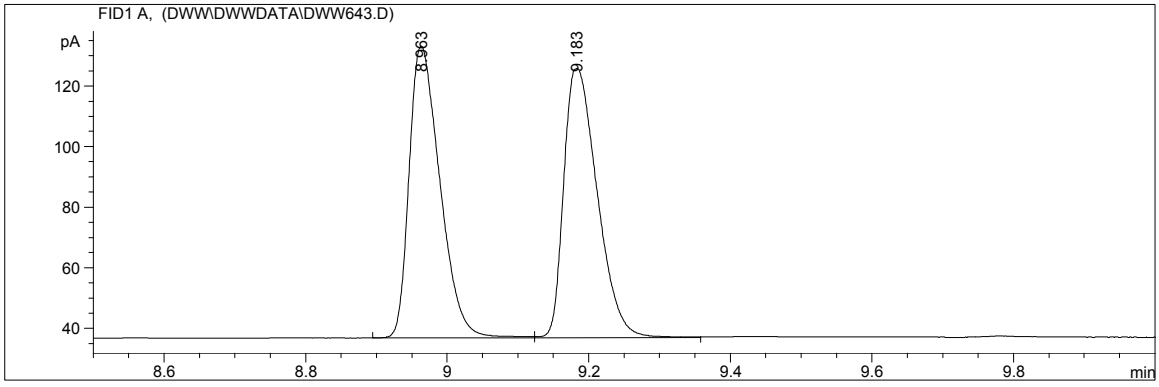
# Catalytic Desymmetrization

# Enantiomeric Excess Assay of Product by Chiral GC

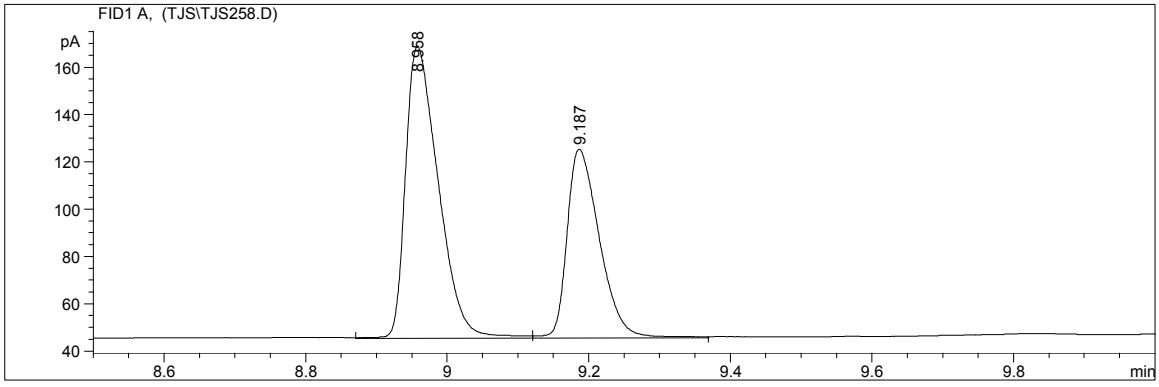



(***S***) **X**

Racemic Product



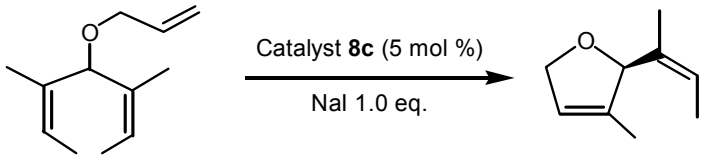

Product from Desymmetrization (23 % ee)




Conditions: 50 to 100 °C, 5 °C/min, 1mL/min flow rate.

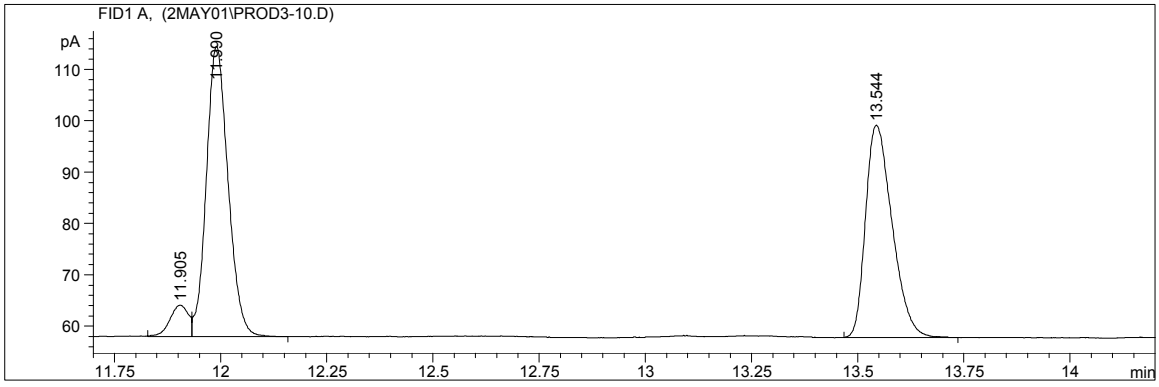
# Catalytic Desymmetrization

# Enantiomeric Excess Assay of Product by Chiral GC

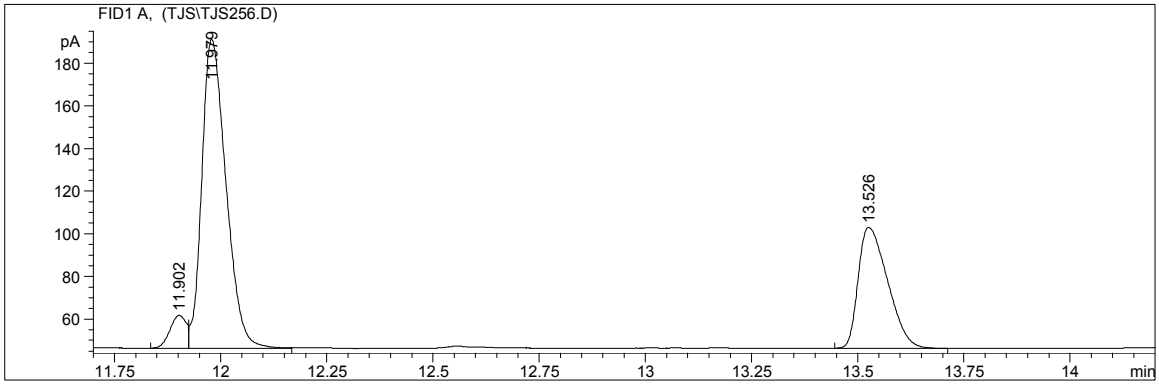



**(*S*) X**

Racemic Product



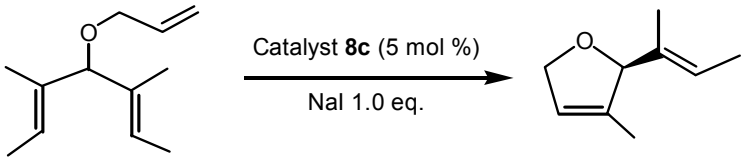

Product from Desymmetrization (35 % ee)




Conditions: 45 to 110 °C, 2 °C/min, 1mL/min flow rate.

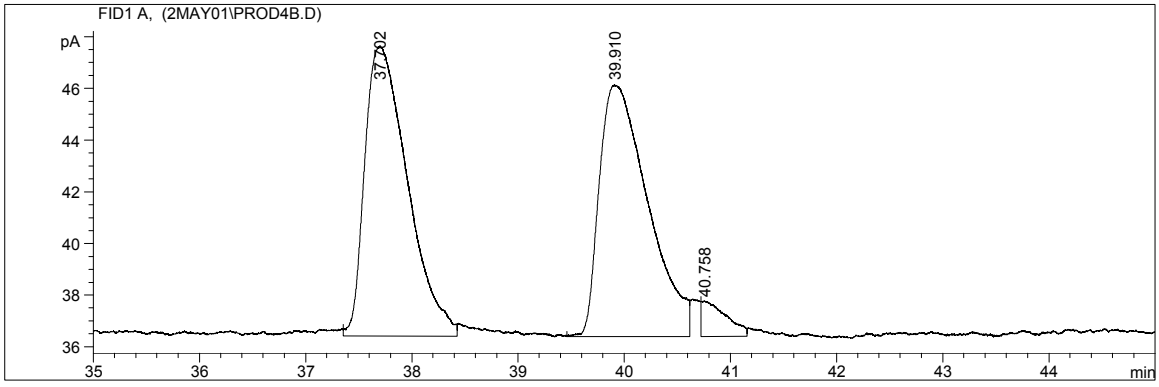
# Catalytic Desymmetrization

# Enantiomeric Excess Assay of Product by Chiral GC

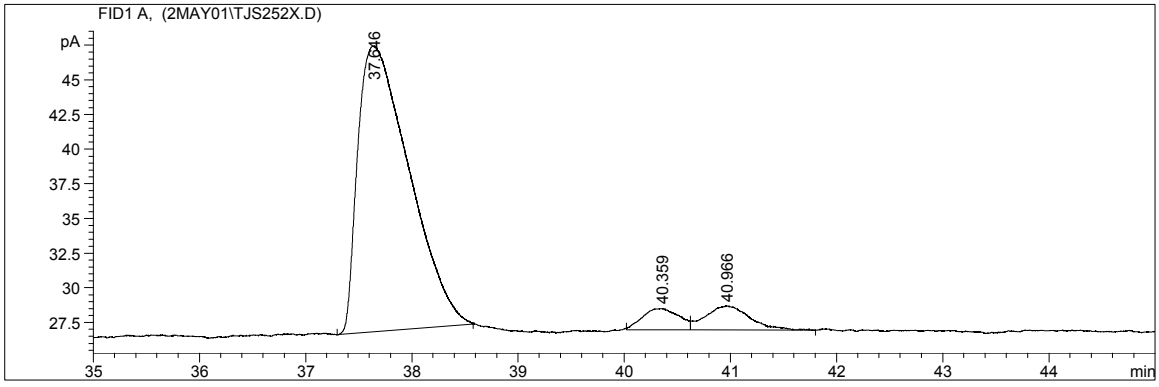



**(*S*) X**

Racemic Product




Product from Desymmetrization (90 % ee)




Conditions: 60 °C, 1mL/min flow rate.